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(54) ELECTROCONDUCTIVE CURABLE RESIN COMPOSITION, ITS CURED PRODUCT AND ITS PRODUCTION METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electroconductive curable resin composition which does not cause the separation of a carbonaceous material from a resin on molding, excels in moldability (compression molding, transfer molding, injection molding, injection compression molding and the like), and obtains a cured product having high electroconductivity, an electroconductive cured product which is obtained by molding the composition and is used for a low-cost fuel cell separator having excellent electroconductivity and heat dissipation and the like, and its production method.

SOLUTION: The electroconductive curable resin and/or the curable resin composition comprises (A) a curable resin and/or a curable resin composition having a viscosity at 80°C of 0.1-1,000 Pas and a viscosity at 100°C of 0.01 to 100 Pas and (B) a carbonaceous material at a mass ratio of component (A) to component (B) of 80-1:20-99. The electroconductive cured product is obtained by molding the composition, and its production method and the fuel cell separator are disclosed.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] This invention relates to the conductive hardenability resin constituent which was excellent in conductivity and heat dissipation nature, and was further excellent in the mold moldability, and its hardening object in more detail about a hardenability resin constituent.

**[0002]**

[Description of the Prior Art] The metal, the carbon material, etc. have been used for the application which needs high conductivity conventionally. Especially the carbon material did not have corrosion like a metal in addition to conductivity, and since it was the ingredient excellent in thermal resistance, lubricity, thermal conductivity, endurance, etc., the important role was come by fields, such as electronics, electrochemistry, energy, and a transportation device, sure enough. And also in a carbon material and the composite material by the combination of polymeric materials, remarkable development was accomplished and one dance of high-performance-izing and the formation of highly efficient nature was borne. That the degree of freedom of fabrication nature improved especially by compound-ization with polymeric materials is one reason the carbon material has developed in each field as which conductivity is required.

[0003] Although a fuel cell generates electricity by the reverse reaction of electrolysis from a viewpoint of an environmental problem and energy problems using hydrogen and oxygen, there are no excretions other than water and it is observed as a clean power plant in recent years, a carbon material and polymeric materials can bear a big role also here. Especially, the polymer electrolyte fuel cell is the most promising as an automobile or a noncommercial use in order to operate at low temperature. Said fuel cell can attain a generation of electrical energy of high power by carrying out the laminating of the single cel which consisted of the solid polymer electrolyte, a gas diffusion electrode, a catalyst, and a separator.

[0004] High conductivity is required, in order that there may be a slot to which fuel gas and oxidant gas are usually supplied, and the high gas impermeability which can separate these gas completely may be required and the separator used here in order to divide this single cel may make internal resistance small. Furthermore, to excel in thermal conductivity, endurance, reinforcement, etc. is demanded.

[0005] This separator has been conventionally examined from both sides of a metal and a carbon material in order to attain these demands. Although the attempt which makes a front face cover noble metals and carbon has been carried out from the problem of corrosion resistance [ metal ], sufficient endurance is not acquired but the cost which starts covering further becomes a problem.

[0006] The glassy carbon which calcinates the mold goods obtained by examination also accomplishing many carbon materials and carrying out press forming of the expanded graphite sheet, the mold goods which the carbon sintered compact infiltrated resin and were stiffened, and thermosetting resin, and is obtained on the other hand, the mold goods which carried out mixed postforming of carbon powder and the resin are raised as an example.

[0007] For example, from the problem of dependability and dimensional accuracy, binding material is

added to carbonaceous powder, after [ heating mixing ] CIP shaping is carried out at JP,8-222241,A, it sinks into the isotropic graphite material which subsequently calcinated and graphitized and was obtained, hardening processing of the thermosetting resin is carried out at it, and the complicated process of carving a slot by cutting is indicated. Moreover, carrying out laminating sticking by pressure after sinking in, and calcinating thermosetting resin on the paper containing carbon powder or a carbon fiber, is indicated by JP,60-161144,A.

[0008] Carrying out injection molding of the phenol resin to the metal mold of a separator configuration, and calcinating it is indicated by JP,2001-68128,A. Although the ingredient by which baking processing was carried out like these examples shows high conductivity, the time amount which baking takes is long and it is deficient in productivity. And since mass-production nature is high cost deficiently further when cutting is required, there are many fields difficult as an ingredient which will spread in the future.

[0009] Although the mold fabricating method is considered as a means by which mass-production nature can expect low cost highly on the other hand, as an ingredient applicable to it, the composite of a carbonaceous ingredient and resin is common. For example, the separator with which the bipolar separator to which the separator which consists of thermosetting resin, such as phenol resin, a graphite, and carbon becomes JP,57-42157,B from thermosetting resin, such as an epoxy resin, and conductive matter, such as graphite, comes to blend expanded graphite and carbon black with thermosetting resin, such as phenol resin and furan resin, at JP,1-311570,A is indicated by JP,58-53167,A, JP,60-37670,A, JP,60-246568,A, JP,64-340,B, and JP,6-22136,B.

[0010]

[Problem(s) to be Solved by the Invention] However, in the composite of a carbonaceous ingredient and resin, since high conductivity was made to discover, the fill of a carbonaceous ingredient needed to be increased sharply, but in order to hold a mold moldability, conductivity high enough was not able to be acquired from making [ many ] the content of resin.

[0011] Moreover, although hardenability resin with viscosity low as much as possible was used in order to raise a mold moldability, since a functional group did not exist in a front face, even if, as for that by which especially the carbonaceous ingredient was also graphitized by altitude, it performed surface treatment, the adhesion with resin hardly went up, but resin and a carbonaceous ingredient dissociated at the time of shaping, and uniform mold goods were not obtained. Although the approach of thickening the viscosity of resin with a thickener was indicated in the PCT/US 00/No. 06999 official report as a means to control the separation, in order to reconcile still higher conductivity and a good mold moldability, it was not enough just to add a thickener.

[0012] Furthermore, in order to acquire high conductivity, when the process of baking which performs prolonged heating for a Plastic solid at a 1000-3000-degree C elevated temperature was included, while the time amount which manufacture takes became long, there was also a problem that a production process will become complicated and cost will go up.

[0013] This invention is made in view of this situation, and does not have the separation at the time of the fabrication of a carbonaceous ingredient and resin, it excels in mold moldabilities (compression molding, transfer molding, injection molding, injection compression molding, etc.), and the conductive hardenability resin constituent with which a conductive high hardening object is acquired is offered. Furthermore, it aims at offering the low cost separator for fuel cells excellent in the conductivity and heat dissipation nature which are obtained by carrying out mold shaping of this constituent, and its manufacture approach.

[0014]

[Means for Solving the Problem] the conductive hardenability resin constituent which has the conductivity in which was excellent in the mold moldability and the hardening object was excellent, and was [ that this invention person should solve the above-mentioned technical problem ] excellent in heat dissipation nature wholeheartedly by using the hardenability resin and/or the hardenability resin constituent which have a certain specific viscosity property as a result of research -- it came to develop.

[0015] Moreover, with the combination of the specific carbon material and this hardenability resin constituent containing boron, it have high conductivity further and came to complete a header and this

invention for a conductive hardening object applicable to the separator for fuel cells, the object for capacitors or the various charge collectors for cells, an electromagnetic wave shielding material, an electrode, a heat sink, a radiator article, electronics components, semi-conductor components, bearing, a PTC component, or a brush, and its manufacture approach.

[0016] That is, this invention relates to the following matters.

[1] (A) Conductive hardenability resin constituent with which viscosity [ in / in the viscosity in 80 degrees C / 0.1 - 1000 Pa-s and 100 degrees C ] is characterized by including the hardenability resin and/or hardenability resin constituent, and (B) carbonaceous ingredient of 0.01 - 100 Pa-s at a rate of 80-1:20-99 with the mass ratio of the (A) component and the (B) component.

A conductive hardenability resin constituent given in the above [1] whose minimum viscosity of the hardening curve in the range of 40-200 degrees C of [2 (A)] components is characterized by being 0.01 - 100 Pa-s the condition for programming-rate/of 20 degrees C.

[0017] The above [1] characterized by being one or more sorts chosen from the group which [3 (B)] components become from a natural graphite, an artificial graphite, expanded graphite, carbon black, a carbon fiber, a gaseous-phase method carbon fiber, and a carbon nanotube, or a conductive hardenability resin constituent given in [2].

A conductive hardenability resin constituent given in the above [3] whose [4 (B)] components are characterized by being a natural graphite, an artificial graphite, a gaseous-phase method carbon fiber, or a carbon nanotube.

[0018] The above [1] characterized by the powder electrical-and-electric-equipment specific resistance of the (B) component of the direction of a right angle being below 0.1-ohmcm to the pressurization direction in the condition of having pressurized so that the bulk density of the carbonaceous ingredient of [5 (B)] components might serve as 1 g/cm<sup>3</sup> thru/or a conductive hardenability resin constituent given in either of [4].

The above [1] characterized by the carbonaceous ingredient of [6 (B)] components containing the boron of 0.05 mass % - 10 mass % thru/or a conductive hardenability resin constituent given in either of [5].

[0019] [7] The conductive hardening object which comes to fabricate a conductive hardenability resin constituent the above [1] thru/or given in either of [6] by the approach of either compression molding, transfer molding, injection molding or injection compression molding.

[8] A conductive hardening object given in the above [7] characterized by volume resistivity being below 2x10-2ohmcm.

[0020] [9] The above [7] characterized by contact resistance being two or less 2x10-2ohmcm, or a conductive hardening object given in [8].

[10] The above [7] characterized by thermal conductivity being 1.0 or more W/m-K thru/or a conductive hardening object given in either of [9].

[11] The above [7] characterized by containing boron of 0.1 or more ppm thru/or a conductive hardening object given in either of [10].

[0021] [12] The manufacture approach of the conductive hardening object characterized by coming to fabricate the above [1] thru/or a conductive hardenability resin constituent given in either of [11] by the approach of either compression molding, transfer molding, injection molding or injection compression molding.

[13] The manufacture approach of a conductive hardening object given in the above [12] whose conductive hardenability resin constituent is characterized by having the shape of a grinding article, a pellet, or a sheet.

[14] The above [12] characterized by fabricating the inside of metal mold, or the whole metal mold by the vacua, or the manufacture approach of a conductive hardening object given in [13].

[0022] [15] The approach of injecting while closing the approach and 2 metal mold which injection compression molding injects and closes where 1 metal mold is opened, the above [12] which is either of the approaches of lasting the mold clamp force after making the mold clamp force of the closed metal mold into zero and injecting it three, or the manufacture approach of a conductive hardening object given in either of [14].

[16] The manufacture approach of a conductive hardening object given in the above [13] which a sheet fabricates by the approach of extrusion molding, roll forming, calender shaping, or compression molding, and is characterized by for thickness being 0.5-5mm and width of face being 20-1000mm.

[0023] [17] The separator for fuel cells which becomes the above [1] thru/or either of [11] from the conductive hardening object of a publication, the object for capacitors or the various charge collectors for cells, an electromagnetic wave shielding material, an electrode, a heat sink, a radiator article, electronics components, semi-conductor components, bearing, a PTC component, or a brush.

[18] The separator for fuel cells which it comes to manufacture by the manufacture approach the above [12] thru/or given in either of [16].

[19] The separator for fuel cells given in the above [18] whose thickness of the thinnest part it has four or more through tubes, a slot with a width of face [ of 0.2-2mm ] and a depth of 0.2-1.5mm is located to both sides of a separator, and is characterized by 1mm or less and specific gravity being [ 1.7 or more and permeability ] below  $1 \times 10^{-6} \text{ cm}^2/\text{sec}$ .

[0024]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. As for the hardenability resin and/or the hardenability resin constituent of the (A) component in this invention, it is desirable that viscosity [ in / in the viscosity in 80 degrees C / 0.1 - 1000 Pa-s and 100 degrees C ] is 0.01 - 100 Pa-s. More preferably, viscosity [ in / in the viscosity in 80 degrees C / 1 - 500 Pa-s and 100 degrees C ] is 0.01 - 50 Pa-s, and viscosity [ in / in the viscosity in 80 degrees C / 1 - 100 Pa-s and 100 degrees C ] is 0.1 - 10 Pa-s still more preferably.

[0025] Since resin and a carbon system filler dissociate [ viscosity / in / in the viscosity in 80 degrees C / 0.1 or less Pa-s and/or 100 degrees C ] by 0.01 or less Pa-s at the time of fabrication and poor shaping becomes easy to take place, it is not desirable. Moreover, since viscosity is high in 100 or more Pa-s, viscosity [ in / in the viscosity in 80 degrees C / 1000 or more Pa-s and/or 100 degrees C ] of a fluidity is bad, it is hard coming to fabricate especially the product of thin meat, and a desired hardening object is not acquired.

[0026] Furthermore, in this invention, it is desirable that the minimum viscosity of the hardening curve in the range of 40-200 degrees C of the (A) component is the bottom of programming-rate the condition for /of 20 degrees C and 0.01 - 100 Pa-s. More preferably, it is 0.01 - 50 Pa-s, and is 0.1 - 10 Pa-s still more preferably. Since the minimum viscosity of viscosity of the hardening curve in the range of 40-200 degrees C is too low in 0.01 or less Pa-s under programming-rate the condition for /of 20 degrees C, it is not enough for resin and a carbon system filler to dissociate at the time of shaping, and carry out mold shaping, and in 100 or more Pa-s, since viscosity is too high, a fluidity cannot say it as bad sufficient process condition.

[0027] The viscosity and the hardening property of the (A) component of this invention were measured using the rheometer MCR 300 made from FIJIKA. Specifically, measurement of viscosity performs static viscoelasticity measurement using a cone plate (CP25) on gap 0.5mm, rate of strain 1 (1/S), the measurement temperature of 80 degrees C, and 100-degree C conditions.

[0028] On the other hand, using a parallel plate (PP25), a hardening property performs dynamic viscoelasticity measurement the condition for gap 1mm, amplitude [ of 20% ], frequency [ of 10Hz ], measurement temperature requirement [ of 40-200 degrees C ], and programming-rate/of 20 degrees C, and measures the minimum viscosity of a hardening curve.

[0029] As hardenability resin of the (A) component used in this invention, phenol resin, an unsaturated polyester resin, an epoxy resin, vinyl ester resin, alkyd resin, acrylic resin, melamine resin, xylene resin, guanamine resin, diallyl phthalate resin, allyl ester resin, furan resin, imide resin, urethane resin, a urea resin, etc. are mentioned.

[0030] It is desirable that it is at least one sort of hardenability resin chosen from phenol resin, an unsaturated polyester resin, an epoxy resin, vinyl ester resin, and allyl ester resin also in these.

Furthermore, in the field as which thermal resistance, acid resistance, etc. are required, the resin which has the structure of a ring type like the isocyclic ring and heterocycle in a molecule frame is desirable.

[0031] As resin which has ring type structure in a molecule frame, when unsaturated polyester and vinyl

ester resin of for example, a bisphenol system, novolak mold vinyl ester resin, allyl ester resin, diallyl phthalate resin, etc. are included, it is desirable at the point that the thermal resistance of the conductive hardening object acquired, chemical resistance, and hot water resistance can be improved. The hardenability resin which has the molecular structure containing a fluorine in the application as which long-term hot water resistance is required is the most desirable.

[0032] Moreover, at least one or more sorts further chosen from a reactant monomer, lubricant, a thickener, a cross linking agent, a bridge formation assistant, a hardening initiator, a hardening accelerator, a concrete retarder, a plasticizer, a low contraction agent, a CHIKUSO agent, a surfactant, a solvent, etc. may be included in the hardenability resin constituent of the (A) component besides the hardenability resin indicated above.

[0033] Although there will be especially no limitation as a carbonaceous ingredient of the (B) component in this invention if carbonized; at least one or more sorts chosen from the group which consists of a natural graphite, an artificial graphite, expanded graphite, carbon black, a carbon fiber, a gaseous-phase method carbon fiber, and a carbon nanotube, for example are used. A natural graphite, an artificial graphite, a gaseous-phase method carbon fiber, and a carbon nanotube are used especially preferably.

[0034] As for the carbonaceous ingredient of the (B) component used in this invention, it is desirable for the powder electrical-and-electric-equipment specific resistance of the direction of a right angle to be low as much as possible to the pressurization direction when making bulk density into 1 g/cm<sup>3</sup>, and it is below 0.07-ohmcm more preferably below 0.1-ohmcm. (B) When the electric specific resistance of the carbonaceous ingredient of a component exceeds 0.1-ohmcm, the conductivity of the hardening object hardened and acquired becomes low, and there is an inclination for a desired hardening object not to be acquired.

[0035] As an example of the carbonaceous ingredient of the (B) component used in this invention, the measuring method of the electric specific resistance at the time of using graphite powder is shown in drawing 1. A cradle and 4 are side frames and the electrode with which 1 and 1' consists of a copper plate in drawing 1, the compression rod with which 2 consists of resin, and 3 all consist of resin. 5 is the graphite powder of a sample. 6 is the lower limit of a sample and is a potential tap prepared in the vertical center section at space.

[0036] Using the four probe method shown in this drawing 1, as it is the following, the electric specific resistance of a sample is measured. A sample is compressed with the compression rod 2. A current (I) is passed from an electrode 1 to electrode 1'. The electrical potential difference between terminals (V) is measured with a terminal 6. At this time, an electrical potential difference uses the value when making a sample into bulk density 1.5 g/cm<sup>3</sup> with a compression rod.

[0037] It will become  $R=V/I$  if the electric resistance (between terminals) of a sample is set to R (omega). [rho which can ask for electric specific resistance by  $\rho=R \cdot S/L$  from now on: The cross section (cm<sup>2</sup>) of the direction of a right angle and L are the distance between terminals 6 (cm) to electric specific resistance and the energization direction of S= sample, i.e., the pressurization direction.]. For a sample, as for the cross section of the direction of a right angle, in actual measurement, width is [ about 1cm and the length (height) of the distance between 0.5cm - 1cm the energization lay length of 4cm, and a terminal (L) ] 1cm.

[0038] Next, the case where an artificial graphite is used is explained as an example of the carbonaceous ingredient of the (B) component used in this invention. In order to obtain an artificial graphite, corks are usually manufactured first. In the raw material of corks, a petroleum system pitch, the pitch of a coal system, etc. carbonize these raw materials, and consider as corks at it. The approach of grinding the burned product (corks and this burned product being set below, and "it being called corks etc.") which fabricated and calcinated the binder moreover in the approach of pulverizing after graphitizing the approach and the corks itself which generally carries out after [ grinding ] graphitization processing of the corks, in order to obtain graphitization powder from corks, or corks after graphitization processing, and using as powder etc. is mentioned. As much as possible, the corks of a raw material etc. have that good from which a crystal has not developed, and 2000 degrees C or less of things more preferably heat-

treated below 1200 degrees C are preferably suitable for them.

[0039] A high-speed tumbling mill (a hammer mill, a pin mill, cage mill), various ball mills (a tumbling mill, a vibration mill, planetary mill), a stirrer mill (a bead mill, attritor, a flow conduit mold mill, ANYURAMIRU), etc. can be used for grinding of (B) carbonaceous ingredients, such as corks and a natural graphite. Moreover, it is usable by selecting conditions also with the screen mill of a pulverizer, a turbo mill, a super micron mill, and a jet mill. (B) carbonaceous ingredients, such as corks and a natural graphite, can be ground using these grinders, powder can be classified according to selection of the grinding conditions in that case, and the need, and mean particle diameter and particle size distribution can be controlled.

[0040] although which approach may be used as an approach of classifying (B) carbonaceous ingredient powder, such as corks and a natural graphite, as long as separation is possible -- a part for an arrow -- a way -- air-current classifiers, such as a forced vortex style mold centrifugal classifier (a micron separator, TABOPU REXX, a turbo KURASHI fire, super separator) and an inertial classifier (advanced bar CHUUARU impactor, elbow jet), can be used. Moreover, a wet sedimentation method, a wet centrifugal classification method, etc. can be used.

[0041] Furthermore, in order to obtain natural-graphite powder, artificial-graphite powder, etc. of high conductivity in this invention, B simple substance, H<sub>3</sub>BO<sub>3</sub>, B-2 O<sub>3</sub>, B<sub>4</sub>C and BN, etc. are added as a source of boron to the powder before graphitization processing, and it often mixes and graphitizes. If mixing of a boron compound is uneven, graphite powder not only becomes an ununiformity, but possibility of sintering at the time of graphitization will become high. In order to make homogeneity mix a boron compound, as for these sources of boron, it is desirable to use 50 micrometers or less as the powder which has the particle size of 20-micrometer or less extent preferably, and to mix.

[0042] Moreover, although the higher one of the graphitization temperature of powder including the source of boron is desirable, since there is constraint of equipment etc., the range of 2500-3200 degrees C is desirable. Although there is especially no limitation, the approach using the Atchison furnace which puts powder into a graphite crucible and energizes it directly, the method of heating powder with a graphite heating element, etc. can be used for the graphitization approach.

[0043] The expanded graphite powder used as a (B) carbonaceous ingredient in this invention For example, carry out immersion processing of the graphite with which the crystal structure developed into the altitude of a natural graphite, pyrolytic graphite, etc. at the solution of a strong oxidizing quality of the mixture of concentrated sulfuric acid and a nitric acid, and the mixture of concentrated sulfuric acid and hydrogen peroxide solution, and rapid heating is carried out, after making a graphite lamellar compound generate and rinsing. They are the powder obtained by carrying out expansion processing of the C shaft orientations of a graphite crystal, and the powder which ground what rolled it out in the shape of a sheet once.

[0044] As a carbon fiber furthermore used as a (B) carbonaceous ingredient, the pitch system made from heavy oil, a byproduct oil, a coal tar, etc. and the PAN system made from a polyacrylonitrile are mentioned.

[0045] (B) With the gaseous-phase method carbon fiber used as a carbonaceous ingredient, it is obtained by making a raw material carry out the pyrolysis reaction of the organic compounds, such as benzene, toluene, and natural gas, at 800-1300 degrees C with hydrogen gas under existence of transition metal catalysts, such as a ferrocene. Furthermore, what carried out graphitization processing at about 2500-3200 degrees C after that is desirable. Graphitization processing is more preferably carried out at about 2500-3200 degrees C with graphitization catalysts, such as boron, boron carbide, beryllium, aluminum, and silicon.

[0046] It is desirable to use a gaseous-phase method [ the diameter of fiber is 0.05-10 micrometers, and fiber length is 1-500 micrometers ] carbon fiber as a gaseous-phase method carbon fiber used in this invention. As a more desirable diameter of fiber, it is 0.1-5 micrometers and is 0.1-0.5 micrometers still more preferably. Fiber length is 5-100 micrometers more preferably, and is 10-20 micrometers still more preferably.

[0047] (B) With the carbon nanotube used as a carbonaceous ingredient, not only the mechanical

strength but a field emission function and a hydrogen absorption function attract attention on industry in recent years, and their eyes are beginning to be further turned also to a magnetic function. This kind of carbon nanotube is called a graphite whisker, filler MENTASU carbon, a graphite fiber, a super-thin carbon tube, a carbon tube, carbon fibril, the carbon micro tube, the carbon nano fiber, etc.

[0048] The graphite film which forms a tube appears in a carbon nanotube further, and there are a certain monolayer carbon nanotube and a multilayer carbon nanotube which is a multilayer as it. In this invention, although it is both usable, the hardening object of conductivity with higher using a monolayer carbon nanotube preferably or a mechanical strength is acquired.

[0049] A carbon nanotube is obtained by refining with a hydrothermal method, a centrifuge method, ultrafiltration, an oxidation style, etc., in order to produce for example, to the Corona Publishing publication "the foundation of a carbon nanotube" (P23 - 57 or P1998 issue) with an arc discharge method, a laser evaporation method, a thermal decomposition method, etc. of a publication and to raise purity to it further.

[0050] More preferably, in order to remove an impurity, high temperature processing is carried out in an about 2500-3200-degree C inert gas ambient atmosphere. It is good to carry out high temperature processing at about 2500-3200 degrees C among an inert gas ambient atmosphere with graphitization catalysts, such as boron, boron carbide, beryllium, aluminum, and silicon, still more preferably.

[0051] In this invention, it is desirable to use the carbon nanotube whose diameter of fiber is 0.5-100nm and whose fiber length is 0.01-10 micrometers, 1-10nm of more desirable diameters of fiber is 1-5nm still more preferably, and more desirable fiber length is 0.05-5 micrometers, and is 0.1-3 micrometers still more preferably.

[0052] The diameter of fiber of the gaseous-phase method carbon fiber and carbon nanotube which are used in this invention, and fiber length can be measured with an electron microscope.

[0053] As carbon black used in this invention, incomplete combustion, such as natural gas, the KETCHIEN black obtained by the pyrolysis of acetylene, acetylene black, the furnace carbon obtained by the incomplete combustion of a hydrocarbon oil or natural gas, the thermal carbon obtained by the pyrolysis of natural gas are mentioned.

[0054] Moreover, as for the boron contained in the carbonaceous ingredient of the (B) component of this invention, it is desirable 0.05 mass %-10 mass % To be contained in a carbon material. The target graphite powder of high conductivity may not be obtained for the amount of boron under by 0.05 mass %. Even if the amount of boron is contained exceeding 10 mass %, the improvement effect of the conductive improvement in a carbon material is small.

[0055] (B) For example, items, such as a natural graphite, an artificial graphite, expanded graphite, carbon black, a carbon fiber, a gaseous-phase method carbon fiber, and a carbon nanotube, or one or more sorts of those mixture can be made to contain as an approach of making the carbonaceous ingredient of a component containing boron, by adding B simple substance, B<sub>4</sub>C, BN, and B<sub>2</sub>O<sub>3</sub>, and H<sub>3</sub>B<sub>0</sub>3 grade, often mixing as a source of boron, and carrying out graphitization processing at about 2500-3200 degrees C.

[0056] If mixing of a boron compound is uneven, graphite powder not only becomes an ununiformity, but possibility of sintering at the time of graphitization will become high. In order to mix homogeneity, as for these sources of boron, it is desirable to use 50 micrometers or less as the powder which has the particle size of 20-micrometer or less extent preferably, and to mix to powder, such as corks.

[0057] (B) When not adding boron into the carbonaceous ingredient of a component, if it graphitizes, a degree of graphitization (degree of crystallinity) will fall, a lattice spacing becomes large, and the graphite powder of high conductivity is not obtained. moreover, boron and/or a boron compound mix the gestalt of content of boron in a graphite -- even having -- although it will not matter if it is, it is mentioned as what also has what exists between the layers of a graphite crystal more suitable and the more suitable thing by which some carbon atoms which form a graphite crystal were permuted by the boron atom. Moreover, association of a boron atom when some carbon atoms are permuted by the boron atom, and a carbon atom may be what kind of joint formats, such as covalent bond and ionic bond.

[0058] The hardenability resin of the (A) component of this invention, and/or a hardenability resin

constituent and the carbonaceous ingredient of the (B) component are mass ratios, and are the rate of 80-1:20-99. (A) If the addition of a component exceeds 80 mass % and the (B) carbon material becomes under 20 mass %, since the conductivity of a hardening object becomes low, it is not desirable.

[0059] Furthermore, to the conductive hardenability resin constituent of this invention, it is the purpose which improves a degree of hardness, reinforcement, conductivity, a moldability, endurance, weatherability, a water resisting property, etc., and additives, such as glass fiber, organic fiber, UV stabilizer, an anti-oxidant, a defoaming agent, a leveling agent, a release agent, lubricant, water repellent, a thickener, a low contraction agent, and a hydrophilic grant agent, can be added further.

[0060] It is desirable to mix homogeneity if possible, keeping it constant at the temperature which uses the mixer and kneading machine which are generally used in each above-mentioned component in the pitch fields, such as a roll, an extruder, a kneader, a Banbury mixer, a Henschel mixer, and a planetary mixer, and hardening does not start, in order to obtain the conductive hardenability resin constituent of this invention. Moreover, when adding organic peroxide, after mixing all other components to homogeneity, it is good to add organic peroxide finally and to mix.

[0061] After kneading or mixing, the conductive hardenability constituent of this invention is the purpose made easy, and can grind or corn ingredient supply in a mold making machine metallurgy mold.

[0062] It is desirable to grind cooling in order to be able to use a homogenizer, the Wiley grinder, a high-speed tumbling mill (a hammer mill, a pin mill, a cage mill, blender), etc. for grinding of a conductive hardenability constituent and to prevent condensation of ingredients. The approach of pelletizing using an extruder, RUDA, a ko kneader, etc. or a pan mold granulating machine is used for a granulation.

[0063] As an approach of carrying out mold shaping of the conductive hardenability constituent of this invention, compression molding, transfer molding, injection molding, or injection compression molding is used. Preferably, at the time of various fabrication, the inside of metal mold or the whole metal mold is made into a vacua, and is fabricated.

[0064] In order to raise a molding cycle in compression molding, it is desirable to use multi-cavity mold. Still more preferably, if the multi-platen press (laminating press) approach is used, many products can be fabricated with a small output. In order to raise profile irregularity with a plane product, pressing, once it fabricates a non-hardened sheet is desirable.

[0065] In injection molding, it is the purpose which raises a moldability further, and carbon dioxide gas is poured in from the middle of a making machine cylinder, and it melts into an ingredient, and can fabricate in the supercritical condition. In order to raise the profile irregularity of a product, it is desirable to use the injection compression approach.

[0066] The approach of closing, while injecting where the approach or 3 metal mold to which metal mold is shut is opened after injecting an ingredient, where the approach and 2 metal mold which are injected in the state of the mold clamp force 0 as a injection compressing method where 1 metal mold is closed are opened to a position etc. can be used.

[0067] It is important for a die temperature to embrace the class of constituent, and to select and search for optimum temperature. Although suitably selected by the class of ingredient, for example in a 120-200-degree C temperature requirement, it can determine in range called for [ for / 30 seconds / - ] 1200 seconds. When the hardenability resin of radical reaction nature, an epoxy resin, phenol resin, etc. are used especially, for 30 - 120 seconds is desirable in 150-180 degrees C. Moreover, perfect hardening can be carried out after hardening by giving after-cure for 10 minutes - for 600 minutes in a 150-200-degree C temperature requirement. After-cure can control the curvature of a product by carrying out by pressurizing 5 or more MPas.

[0068] What has the property described below as a conductive hardening object of this invention is desirable. That is, below  $2 \times 10^{-2}$  ohm cm of volume resistivity is desirable, it is below  $8 \times 10^{-3}$  ohm cm more preferably, and below  $5 \times 10^{-3}$  ohm cm is especially used for the application of the separator for fuel cells, the object for capacitors or the various charge collectors for cells, an electromagnetic wave shielding material, an electrode, a heat sink, a radiator article, electronics components, semi-conductor

components, bearing, a PTC component, or a brush suitably.

[0069] Two or less 2x10-2ohmcm is desirable, contact resistance is two or less 1x10-2ohmcm more preferably, and two or less 7x10-3ohmcm is especially suitable for it. 1.0 or more W/m-K is desirable, thermal conductivity is 4.0 or more W/m-K more preferably, and 10 or more W/m-K is especially suitable for it.

[0070] Moreover, as for the conductive hardening object of this invention, it is desirable to contain boron 0.1 ppm or more. It is 0.5 ppm or more more preferably, and is 1 ppm or more still more preferably. There is an inclination for conductivity with the content of boron high in less than 0.1 ppm not to be acquired.

[0071] The hydrometry of the separator for fuel cells of this invention is JIS. It measures according to A law (underwater substitution method) of K7112. Moreover, a permeability measuring method is JIS. Based on K7126A law, it measures using gaseous helium at 23 degrees C.

[0072] Moreover, since mold shaping is easy for the conductive hardenability resin constituent of this invention, it is the optimal as a composite material of the field of which thickness precision is required like the separator for fuel cells. Furthermore, the hardening object can reproduce the conductivity and thermal conductivity of a graphite infinite, and a very highly efficient thing is obtained in that it excels in thermal resistance, corrosion resistance, shaping precision, etc.

[0073] Therefore, it is useful for each application, such as various components, such as the electronics field, electrical machinery, a machine, and a vehicle, and is especially mentioned as a suitable ingredient for the object for capacitors or the various charge collectors for cells, an electromagnetic wave shielding material, an electrode, a heat sink, a radiator article, electronics components, semi-conductor components, bearing, a PTC component, a brush, or the separator for fuel cells.

[0074]

[Example] Although an example explains this invention further below at a detail, this invention is not limited to these examples at all. The used ingredient is shown in Table 1.

[0075]

[Table 1]

(A) 成分(硬化性樹脂及び/、硬化性樹脂組成物)

		A1	A2	A3	A4	A5
アリエヌテル樹脂(昭和電工株製)	AC701	70				
アリエヌテル樹脂(昭和電工株製)	AP001		100	70		
不飽和ポリエステル樹脂(日本エビ化成製)	ユピカ8524	30		30		100
ビニルエステル樹脂(昭和高分子㈱製)	H-600				100	
シクミルバーオキサイド(日本油脂㈱製)	バーコミルD	2	2	2	2	2
試薬(純正化学㈱製)	ステアリン酸	2	2	2	2	2
試薬(純正化学㈱製)	ステアリン酸亜鉛	3	3	3	3	3
<hr/>						
粘度 (Pa·s)	80°C	20.4	11.2	203	0.067	11800
	100°C	3.74	1.76	12.4	0.027	820
<hr/>						
硬化曲線の最低粘度(40~200°C)						
		1.21	0.81	4.96	0.0098	188

[0076] For the measurement of viscosity of hardenability resin and/or a hardenability resin constituent, and hardening property measurement, it measured using the rheometer MCR 300 made from FIJIKA. Measurement of viscosity performed static measurement using the cone plate (CP25) on gap 0.5mm, rate of strain 1 (1/s), the measurement temperature of 80 degrees C, and 100-degree C conditions. Using the parallel plate (PP25), the hardening property performed dynamic viscoelasticity measurement the condition for gap 1mm, amplitude [ of 20% ], frequency [ of 10Hz ], measurement temperature [ of 40-200 degrees C ], and programming-rate/of 20 degrees C, and measured the minimum viscosity of a hardening curve.

[0077] (B) Component (carbonaceous ingredient)

B1: Coarse grinding of the LPC-S corks made from Nippon Steel Chemistry which are non-needle coke (\*\*\*\*\*\*) was carried out to the magnitude of 2mm - 3mm or less with the pulverizer [the Hosokawa

Micron CORP. make]. This coarse-grinding article was pulverized with the jet mill (IDS2UR, Product made from Japanese pneumatic one). Then, the classification adjusted to a desired particle size. Particle removal of 5 micrometers or less performed the air-current classification using the turbo KURASHI fire (TC15N, product made from Nissin Engineering).

[0078] 0.6kg (B4C) of boron carbide was added to 14.4kg of a part of this adjusted pulverizing article, and it mixed for 5 minutes by 800rpm with the Henschel mixer. This was enclosed with the graphite crucible with a lid with a bore [ of 40cm ], and a volume of 40l., and it put into the graphitizing furnace using a graphite heater, and graphitized at the temperature of 2900 degrees C under the argon gas ambient atmosphere. Powder was taken out after cooling this radiationally and 14kg powder was obtained. The obtained graphite fines were mean-particle-diameter [ of 20.5 micrometers ], and B content 1.3wt%.

[0079] B-2: Coarse grinding of the LPC-S corks made from Nippon Steel Chemistry (henceforth "Corks A") which are non-needle coke (\*\*\*\*\*\*) was carried out to the magnitude of 2mm - 3mm or less with the pulverizer [the Hosokawa Micron CORP. make]. This coarse-grinding article was pulverized with the jet mill (IDS2UR, Product made from Japanese pneumatic one). Then, the classification adjusted to a desired particle size. Particle removal of 5 micrometers or less performed the air-current classification using the turbo KURASHI fire (TC15N, product made from Nissin Engineering).

[0080] 14.2kg of parts, 0.2kg (the diameter of the VGCF-G ("VGCF" is Showa Denko K.K. trademark.) fiber by Showa Denko K.K. of 0.1-0.3 micrometers, fiber length of 10-50 micrometers) of gaseous-phase method carbon fibers, and 0.6kg (B4C) of boron carbide of this adjusted pulverizing article were mixed for 5 minutes by 800rpm with the Henschel mixer. This was enclosed with the graphite crucible with a lid with a bore [ of 40cm ], and a volume of 40l., and it put into the graphitizing furnace using a graphite heater, and graphitized at the temperature of 2900 degrees C under the argon gas ambient atmosphere. Powder was taken out after cooling this radiationally and 14.1kg powder was obtained. The obtained graphite fines were mean-particle-diameter [ of 19.5 micrometers ], and B content 1wt%.

[0081] B3: 0.15kg (B4C) of boron carbide was mixed with 14.85kg (UFG30) ("UFG" is the Showa Denko K.K. trademark.) of artificial graphites by Showa Denko K.K. for 5 minutes by 800rpm with the Henschel mixer. This was enclosed with the graphite crucible with a lid with a bore [ of 40cm ], and a volume of 40l., and it put into the graphitizing furnace using a graphite heater, and graphitized at the temperature of 2900 degrees C under the argon gas ambient atmosphere. Powder was taken out after cooling this radiationally and 14.4kg powder was obtained. The obtained graphite fines were mean-particle-diameter [ of 12.1 micrometers ], and B content 0.2wt%.

[0082] B4: 0.15kg (B4C) of boron carbide was mixed with 14.85kg (LB-CG) of natural graphites made from a Japanese graphite industry for 5 minutes by 800rpm with the Henschel mixer. This was enclosed with the graphite crucible with a lid with a bore [ of 40cm ], and a volume of 40l., and it put into the graphitizing furnace using a graphite heater, and graphitized at the temperature of 2900 degrees C under the argon gas ambient atmosphere. Powder was taken out after cooling this radiationally and 13.9kg powder was obtained. The obtained graphite fines were mean-particle-diameter [ of 20.6 micrometers ], and B content 0.1wt%.

[0083] B5: Coarse grinding of the corks A was carried out to the magnitude of 2mm - 3mm or less with the pulverizer. This coarse-grinding article was pulverized with the jet mill. Then, the classification adjusted to a desired particle size. Particle removal of 5 micrometers or less performed the air-current classification using the turbo KURASHI fire. This was enclosed with the graphite crucible with a lid with a bore [ of 40cm ], and a volume of 40l., and it put into the graphitizing furnace using a graphite heater, and graphitized at the temperature of 2900 degrees C. After cooling this radiationally, powder was taken out and graphite fines were obtained. The obtained graphite fines were mean-particle-diameter [ of 20.5 micrometers ], and B content 0wt%.

[0084] The measuring method of the physical properties of a hardening object is shown below. Volume resistivity is JIS. Based on K7194, it measured with the four point probe method. A contact resistance value contacts a test piece 11 (20mmx20mmx2mm) and carbon paper 12 (TGP-H -60 by Toray Industries, Inc.) (20mmx20mmx0.1mm) with the equipment shown in drawing 3, sandwiches it with a

copper plate 13, and applies the planar pressure of 1.96MPa. And the constant current of 1A was passed in the penetration direction, and resistance was calculated by contacting a terminal 14 to the interface of a test piece 11 and carbon paper 12, and measuring an electrical potential difference. The cross section in contact with the value was integrated, and it considered as the contact resistance value.

[0085] Flexural strength and a bending elastic modulus are JIS. Based on K6911, the test piece (80mmx10mmx4mm) was measured with the three-point type flexural strength measuring method on condition that span spacing of 64mm, and bending rate 2 mm/min. Sample size was performed by 100x10x1.5mm.

[0086] Using the pressure type kneader (1L), examples 1-7 and the examples 1-2 of a comparison are the conditions of the temperature of 70 degrees C, and rotational frequency 40rpm, and were kneaded for 5 minutes. a constituent -- 80wt(s)% -- it adjusted so that it might fill up. The kneading object was fed into the metal mold which can do a 100x100x1.5mm plate after kneading, it hardened for 5 minutes under the die temperature of 170 degrees C, and the pressurization of 30MPa using 50t compacting machine, and the hardening object was acquired.

[0087] Furthermore, about examples 1-3 and the examples 1-2 of a comparison, the injection-molding test was performed for the plate of the separator configuration which has a letter slot of meandering with a 1mm pitch and a slot depth of 0.5mm in both sides in 120x100x1.5mm size with the die temperature of 160 degrees C, and 75t injection molding machine. The difference in the moldability by the viscosity difference of a thermosetting resin constituent is shown in Table 2.

[0088]

[Table 2]

		実施例1	実施例2	実施例3	比較例1	比較例2
硬化性樹脂組成物	A1	100				
	A2		100			
	A3			100		
	A4				100	
	A5					100
炭素質材料	B1	400	400	400	400	400
体積固有抵抗	$\text{m}\Omega\text{ cm}$	4.1	3.2	5.4	3.6	15
接触抵抗	$\text{m}\Omega\text{ cm}^2$	5.2	3.6	6	10	63
熱伝導率	$\text{W}/\text{mk}$	20	16	14	18	12
曲げ強度	MPa	66	56	57	21	49
曲げ弾性率	GPa	17	16	21	12	19
成形性(円盤フローテスト)*1		○	○	○	×(1)	×(2)
射出成形テスト*2		○	○	○	×	×

\* 1 円盤フローテスト：組成物10gを160°Cに調整されたプレス機へ投入し、18t荷重を

かけたときの材料が広がり(直径)や外観を評価。

○：材料の分離がなく、材料の広がり(直径)110mm以上。

×：材料が分離、若しく材料の広がり(直径)が110mm未満。

×(1)：炭素質材料と硬化性樹脂が分離。

×(2)：流動不足。円盤フロー80mm。

\* 2 ○：両面溝付きセバレーター形状で、成形不良のない製品を得られた。

×：成形不良によりセバレーター形状での製品が得られなかつた。

[0089] In the low viscosity which a carbonaceous ingredient and a thermosetting resin constituent separate, since only resin flowed and a filler remained in the case of fabrication, injection molding was not able to be done. Moreover, when viscosity was too high, since [ that a fluidity was bad ] the cure rate was quick, injection molding was not able to be carried out. It is shown in Table 3 that a conductive high hardened material is obtained by using the carbonaceous ingredient with which boron is contained.

[0090]

[Table 3]

		実施例4	実施例5	実施例6	実施例7
硬化性樹脂相成物	A1	100	100	100	100
樹脂質材料	B2	400			
	B3		400		
	B4			400	
	B5				400
体積固有抵抗	mΩ cm	4	3.5	4	12
接触抵抗	mΩ cm <sup>2</sup>	4.8	3.8	4	18
熱伝導率	W/mk	18	25	20	16
曲げ強度	MPa	62	61	64	58
曲げ弾性率	GPa	19	37	44	18

[0091]

[Effect of the Invention] Since the hardening object is excellent in conductivity and heat dissipation nature, the conductive hardenability resin constituent of this invention The ingredient, for example, electronics field, of the field which was conventionally difficult to realize, Are widely applicable to various application and components, such as an electric product, a machine part, and vehicle components. It is especially useful as a material for separators of fuel cells, such as the object for capacitors or the various charge collectors for cells, an electromagnetic wave shielding material, an electrode, a heat sink, a radiator article, electronics components, semi-conductor components, bearing, a PTC component, a brush, or a polymer electrolyte fuel cell.

[Translation done.]

**\* NOTICES \***

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] (A) The conductive hardenability resin constituent with which viscosity [ in / in the viscosity in 80 degree C / 0.1 - 1000 Pa-s and 100 degrees C ] is characterized by including the hardenability resin and/or hardenability resin constituent, and (B) carbonaceous ingredient of 0.01 - 100 Pa-s at a rate of 80-1:20-99 with the mass ratio of the (A) component and the (B) component.

[Claim 2] (A) The conductive hardenability resin constituent according to claim 1 with which the minimum viscosity of the hardening curve in the range of 40-200 degrees C of a component is characterized by being 0.01 - 100 Pa-s the condition for programming-rate/of 20 degrees C.

[Claim 3] (B) The conductive hardenability resin constituent according to claim 1 or 2 characterized by being one or more sorts chosen from the group which a component becomes from a natural graphite, an artificial graphite, expanded graphite, carbon black, a carbon fiber, a gaseous-phase method carbon fiber, and a carbon nanotube.

[Claim 4] (B) The conductive hardenability resin constituent according to claim 3 with which a component is characterized by being a natural graphite, an artificial graphite, a gaseous-phase method carbon fiber, or a carbon nanotube.

[Claim 5] (B) The conductive hardenability resin constituent according to claim 1 to 4 characterized by the powder electrical-and-electric-equipment specific resistance of the (B) component of the direction of a right angle being below 0.1-ohmcm to the pressurization direction in the condition of having pressurized so that the bulk density of the carbonaceous ingredient of a component might serve as 1 g/cm<sup>3</sup>.

[Claim 6] (B) The conductive hardenability resin constituent according to claim 1 to 5 characterized by the carbonaceous ingredient of a component containing the boron of 0.05 mass % - 10 mass %.

[Claim 7] The conductive hardening object which comes to fabricate a conductive hardenability resin constituent according to claim 1 to 6 by the approach of either compression molding, transfer molding, injection molding or injection compression molding.

[Claim 8] The conductive hardening object according to claim 7 characterized by volume resistivity being below 2x10-2ohmcm.

[Claim 9] The conductive hardening object according to claim 7 or 8 characterized by contact resistance being two or less 2x10-2ohmcm.

[Claim 10] The conductive hardening object according to claim 7 to 9 characterized by thermal conductivity being 1.0 or more W/m-K.

[Claim 11] The conductive hardening object according to claim 7 to 10 characterized by containing boron 0.1 ppm or more.

[Claim 12] The manufacture approach of the conductive hardening object characterized by coming to fabricate a conductive hardenability resin constituent according to claim 1 to 11 by the approach of either compression molding, transfer molding, injection molding or injection compression molding.

[Claim 13] The manufacture approach of a conductive hardening object according to claim 12 that a conductive hardenability resin constituent is characterized by having the shape of a grinding article, a

pellet, or a sheet.

[Claim 14] The manufacture approach of the conductive hardening object according to claim 12 or 13 characterized by fabricating the inside of metal mold, or the whole metal mold by the vacua.

[Claim 15] The approach of injecting while closing the approach and 2 metal mold which injection compression molding injects and closes where 1 metal mold is opened, the manufacture approach of the conductive hardening object according to claim 12 to 14 which is either of the approaches of lasting the mold clamp force after making the mold clamp force of the closed metal mold into zero and injecting it three.

[Claim 16] The manufacture approach of the conductive hardening object according to claim 13 which a sheet fabricates by the approach of extrusion molding, roll forming, calender shaping, or compression molding, and is characterized by for thickness being 0.5-5mm and width of face being 20-1000mm.

[Claim 17] The separator for fuel cells which consists of a conductive hardening object according to claim 1 to 11, the object for capacitors or the various charge collectors for cells, an electromagnetic wave shielding material, an electrode, a heat sink, a radiator article, electronics components, semiconductor components, bearing, a PTC component, or a brush.

[Claim 18] The separator for fuel cells which it comes to manufacture by the manufacture approach according to claim 12 to 16.

[Claim 19] The separator for fuel cells according to claim 18 with which it has four or more through tubes, a slot with a width of face [ of 0.2-2mm ] and a depth of 0.2-1.5mm is located to both sides of a separator, and thickness of the thinnest part is characterized by 1mm or less and specific gravity being [ 1.7 or more and permeability ] below  $1 \times 10^{-6} \text{cm}^2/\text{sec}$ .

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[Translation done.]